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Thermodynamics and Kinetics of the Sulfation of Porous Calcium Silicate

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THERMODYNAMICS AND KINETICS OF THE SULFATION OF POROUS CALCIUM SILICATE

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ABSTRACT

The sulfation of plasma sprayed calcium silicate in flowing SO_2 /air mixtures at 900 and 1000°C has been investigated thermogravimetrically. Reaction products were analyzed using electron microprobe and X-ray diffraction analysis techniques, and results were compared with thermodynamic predictions. The percentage, by volume, of SO_2 in air was varied between 0.036 and 10 percent. At 10 percent SO_2 the weight gain curve displays a concave downward shoulder early in the sulfation process. An analytical model was developed which treats the initial process as one which decays exponentially with increasing time and the subsequent process as one which decays exponentially with increasing weight gain. At lower SO_2 levels the initial rate is controlled by the reactant flow rate. At 1100°C and 0.036 percent SO_2 there is no reaction, in agreement with thermodynamic predictions.

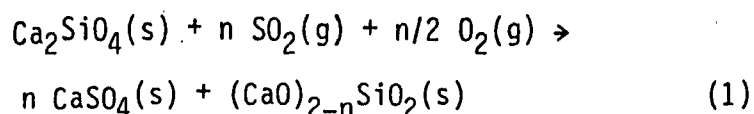
INTRODUCTION

Plasma sprayed calcium silicate, Ca_2SiO_4 , is a potential thermal barrier coating material for gas turbine engine components (1 and 2). These coatings are porous and microcracked which imparts thermal shock resistance to the material. However, the porosity is interconnected so gaseous vapors and molten salt condensates can readily penetrate the coating. It was shown previously that calcium silicate is able to withstand the effects of molten salts better than other thermal barrier coatings. However, gas-borne sulfur oxides react with calcium silicate to form calcium sulfate plus less calcium-rich silicates or silica (3 and 4). Because of this sulfation reaction, calcium silicate and other related materials such as lime, limestone, and cement may, in fact, be used to remove sulfur oxides from combustion gases (e.g., 5-10).

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A general expression for the sulfation reaction is



Thus, the products are CaSO_4 plus $\text{Ca}_3\text{Si}_2\text{O}_7$ when $n=1/2$, CaSiO_3 when $n=1$, or SiO_2 when $n=2$. One may note that as the sulfation products build up on the external and internal surfaces, many of the pores will become clogged. Thus, the changing porosity of the material is expected to affect the sulfation kinetics.

Because sulfation should affect the behavior of a calcium silicate coating, understanding of the sulfation reaction is required for complete understanding of these coatings. Thus, laboratory experiments have been conducted to define the behavior of plasma sprayed calcium silicate in flowing SO_2 /air mixtures at high temperatures. The reaction kinetics were monitored thermogravimetrically, weight gain curves were fit to an analytical model, and product compositions are compared with thermodynamic predictions.

EXPERIMENTAL

Specimens were prepared by plasma spraying commercially prepared calcium silicate powder, -150/+ 400 mesh, onto a smooth stainless steel substrate. The resulting 0.05 cm thick coating was removed mechanically from the substrate. The nitrogen BET surface area of this porous and microcracked material was $0.25 \text{ m}^2/\text{g}$. Wafers of calcium silicate were placed in an open platinum or quartz crucible and heated in a 2.5 cm diameter tube furnace in slowly flowing oxygen. The gas was then switched to SO_2 /air mixtures and the ensuing weight gains were monitored continuously on a Cahn R-100 recording microbalance.

RESULTS AND DISCUSSION

Experimental conditions for 10 sulfation experiments are presented in Table I. Weight gain curves for three of the experiments are presented in Figs. 1a, 1b, and 1c. The first two plots are for experiments 1 and 2, respectively, which were run at the highest SO_2 level employed. The third plot, Fig. 1c for experiment 5, is representative of runs at lower SO_2 levels. In Figs. 1 and 2 the weight gain curves display a shallow concave-downward shoulder at short times. At lower SO_2 levels, such as Fig. 1c, the initial region is linear. As given in Table I and shown in Fig. 2 the initial linear rate, r_0 , for the experiments involving lower SO_2 concentrations, experiments 3 through 9, is

essentially equal to the calculated rate of arrival of gaseous reactant to the specimen surfaces, r_s . This rate was calculated from the flow rate of the air/SO₂ mixture assuming the reactants are $n\text{SO}_2 + n/2 \text{O}_2$ and scaled according to the ratio of the cross sectional area of the crucible to that of the tube. In this linear region the reaction is fast enough to consume essentially all of the sulfur oxides flowing past the calcium silicate. For the conditions of experiment 10, 1100°C and 0.036 percent SO₂, there is no reaction indicating that, under those conditions, CaSiO₄ was more stable than the sulfation products.

For all experiments, except of course experiment 10, the rate of weight gain at long times decays exponentially with increasing weight: i.e.,

$$d(w/w_0)/dt = a' \exp(-b' w/w_0) \quad (2)$$

where w is the weight gained at time t , w_0 is the initial weight, and a' and b' are constants. If it is assumed that this rate law is only obeyed after some time t_1 and corresponding weight gain w_1 , then the appropriate integration is

$$a' \int_{t_1}^t dt = \int_{w_1}^w \exp(b' w/w_0) d(w/w_0) \quad (3)$$

After integrating, the expression becomes

$$w/w_0 = b \ln(at + 1) + c \quad (4)$$

where a , b , and c are constants which can be determined from the weight gain data at $t > t_1$ using regression techniques. The values obtained for the three constants (b , a , and c) for experiments of at least 98 hours duration are presented in Table I. Expression 4 is given in reference 11 for the special case of $t_1 = w_1 = c = 0$, where t is called the "direct logarithmic equation". It is used to describe the oxidation of porous materials according to the so-called "mutually blocking pore" model.

Thus, expression 4 is the direct logarithmic equation modified by the addition of a constant term c . This modified expression only describes the experimental data at t greater than t_1 . As t approaches zero the expression would predict a finite weight gain, c . For the experiments involving 10 percent SO₂, t_1 is approximately equal to the time at the inflection point in the weight gain data, i.e., about 1 or 2 hours. For the other experiments, involving lower levels of SO₂, t_1 is at least 10 hours.

The presence of a shoulder generally indicates that two processes having differing rates are occurring sequentially. The rate of the

second sulfation step is low and so it is not an example of a "breakaway" process such as is discussed in reference 12. Another example of a curve with a shoulder is given in reference 13. There it is shown that under certain conditions a shoulder in weight gain data will appear if the rate of the first process is initially rapid but asymptotically decays to zero. In that example the initial process was sorption of a fluid by a membrane, and the second process involved chemical reaction rate control. In the present example the long-time expression, equation 4, approaches a constant weight gain c , as t approaches zero. (In that respect it is similar to the curve labelled " $d = \infty$ " in Fig. 8.6 of reference 13.) By replacing c in equation 4 by an expression which approaches c asymptotically, a curve with a shoulder is generated. (Fig. 8.5 of reference 13 shows how such an asymptotic curve matches the shoulder at a short time.) The asymptotic equation chosen to describe the early portion of the data is the one parameter sorption equation (13). This expression described the experimental weight gains better than a simple exponential expression. The replacement for c is

$$c \rightarrow c(t) = c \left(1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left(-d (n+1/2)^2 \pi^2 t \right) \right) \quad (5)$$

The adjustable parameter d has units of reciprocal time. An alternate two parameter sorption equation (13) would have given an even better fit; however, the one parameter equation is adequate for the present purposes.

Values of d were obtained by arbitrarily forcing equation 5 to match the experimental data at $w/w_0 = 2/3$ c , $t = t_{2/3}$. One may calculate that at this point

$$d = \frac{0.360}{t_{2/3}} \text{ hours}^{-1} \quad (6)$$

Values of d derived from the data are presented in Table I and the analytical curves are drawn on Figs. 1a through 1c. In Fig. 1c the initial region, where the rate is equal to the reactant flow rate, is taken to be linear (i.e., the slope is unity on the log-log plot).

The analytical curves accurately describe the experimental weight gains. The fit is especially good in the important long-time region where the value of R^2 for the regression exceeds 99.8 percent for all three cases. The fit in the linear portion of Fig. 1c is also very good. For all curves the one-parameter sorption equation becomes asymptotic somewhat sooner than is actually observed. This is primarily due to errors arising from the simplicity of the model.

In experiment 4 all platinum was removed from the reaction system in order to demonstrate the sensitivity of the sulfation reaction to the presence of SO_2 . Earlier it was concluded that at lower SO_2 levels essentially all of the sulfur oxides flowing into the crucible are consumed. At 900°C , even under equilibrium conditions, SO_2 is 6.8 times more abundant than SO_3 . Thus, either the sulfation reaction must involve SO_2 or else that reactant would have to be oxidized rapidly so as to continuously replenish reacted SO_3 . However, in the absence of a catalyst, such as the platinum crucible, SO_2 oxidizes very slowly at 900°C (14). Thus, if sulfation requires gaseous SO_3 , the initial rate should be much lower when the platinum crucible is replaced with a quartz crucible. Comparison of the results of experiments 3 and 4 in Table I and Fig. 2 shows that r_0 was only lowered by a factor of 2 when platinum was removed. This difference is not considered significant because the quartz crucible was smaller in diameter than the platinum crucible (1.0 vs 1.2 cm). Also, the quartz crucible was less open at its base so flow throughout it may have been restricted. Therefore, we conclude that gaseous SO_3 is not required for the sulfation reaction and SO_2 (or perhaps CaSO_3) must oxidize on the specimen surface.

Experiments 5 and 6, listed in Table 1, were run under identical conditions. Normally, the only difference was in the initial weight of calcium silicate, w_0 . Both experiments had the same initial rate, r_0 , when expressed as mg/hr. However, the rates differed at longer times. As a result, whereas w/w_0 was 0.079 after 98 hours in experiment 6, it was only 0.060 after the same time in experiment 5. In both cases the within-experiment precision was very good with values of R^2 of about 99.99 percent. Thus, the within-experiment precision is much higher than the reproducibility. In experiment 6 the calcium silicate was packed rather tightly into the crucible. This may have accounted for much of the observed difference. The BET surface area of the specimen from experiment 6 was measured and found to be $0.14 \text{ M}^2/\text{g}$. This is 56 percent of the value for the as-sprayed material.

X-ray diffraction analysis showed that the powdered starting material best matches the phase $\gamma\text{-Ca}_2\text{SiO}_4$ (JCPDS 24-34). After plasma spraying the material transformed to $\beta\text{-Ca}_2\text{SiO}_4$ (JCPDS 29-371). When exposed to lower SO_2 concentrations for shorter times, the products CaSO_4 (JCPDS 6-226) plus $\text{Ca}_3\text{Si}_2\text{O}_7$ (JCPDS 22-539) predominate. This is shown in Fig. 3a which is a portion of the X-ray diffraction pattern for experiment 5. These are the products when $n=1/2$ in reaction 1. At longer times or higher SO_2 levels CaSO_4 plus CaSiO_3 (JCPDS 27-88) predominate. This is shown in Fig. 3b, the pattern for experiment 2. These products correspond to $n=1$ in equation 1. Changing the temperature from 900 to 1000°C did not significantly change the product composition.

For the experiment 10, run at 1100°C in 0.036 percent SO₂, only β -Ca₂SiO₄ was observed. There was no X-ray evidence that crystalline or amorphous silica (corresponding to n=2 in reaction 1) had formed in any experiment. Neither was there evidence that calcium sulfate had hydrated even after up to a full year of storage.

In Fig. 4a thermodynamic predictions of the value of n in equation 1 are plotted as a function of SO₂ concentration and temperature. For this calculation calcium silicate was taken as the limiting reactant, i.e., SO₂ was greatly in excess. In the present experiments involving flowing SO₂ at constant concentration, this reactant becomes greatly in excess after an infinite amount of time - after an infinite amount of SO₂ had flowed over the calcium silicate. The calculations were performed using the NASA, complex chemical equilibrium computer program (15). Thermodynamic data for calcium sulfate and the calcium silicate species were taken from reference 16. For all calculations, unit activity solid phases are assumed. The calculations show that high temperatures and low SO₂ levels favor no reaction (n=0). At lower temperatures or higher SO₂ levels, n changes first to 1/2, then 1, and finally 2. The observation that there was no reaction in experiment 10 is in accordance with Fig. 4a. However, for all of the other experimental conditions, n tended towards 1/2 at shorter times and lower SO₂ levels, and 1 at longer times and higher SO₂ levels.

Additional thermodynamic calculations help to explain the experimental results. In Fig. 4b the value of n (which, as before, is the ratio of moles of SO₂ consumed per mole of Ca₂SiO₄ consumed) is calculated as a function of temperature and of the ratio of moles of SO₂ initially available for reaction to moles of Ca₂SiO₄ initially available. The calculations pertain specifically to the case of 0.54 percent SO₂ in air. They show that when Ca₂SiO₄ is greatly in excess (the condition at short flow times) a portion of the calcium silicate reacts to give CaSO₄ plus Ca₃Si₂O₇ (n=1/2). Once the reactant ratio passes 1/2, the product CaSiO₃ (n=1) begins to appear. (Although not indicated on Fig. 4b, CaSiO₃ actually begins to occur before all of the Ca₃Si₂O₇ disappears.) Thus, at longer times the reaction for which n=1/2 gives way to n=1. Presumably after very long times, at lower temperatures and higher SO₂ levels, the reaction corresponding to n=2 would begin to occur and silica would be observed.

Cross sections of several specimens were examined by electron microprobe analysis. Fig. 5 shows the results for the specimen exposed to 10 percent SO₂ for 112 hours at 1000°C. This figure shows that the sulfation products form on the external surfaces and on the major pores of the material. (The crack observed in this figure is assumed to have occurred during specimen preparation.)

CONCLUDING REMARKS

In general, the kinetics of calcium silicate formation agree with the kinetics of limestone or lime sulfation as reported in the literature (6-9). That is, the reaction rates are initially high and then slow considerably according to a mechanism involving filling of the porosity by the sulfation products. The exact nature of the initial processes occurring in calcium silicate sulfation are still a matter for conjecture. In the present paper the initial weight gain was described by an asymptotic expression - the sorption equation. The weight gains appear to be too large for the initial process to involve chemical or physical absorption. Chemical absorption ceases after a monolayer of coverage. Physical absorption can continue beyond this point at room temperature (17), but it should be less important at high temperatures. One may calculate, using the measured BET surface area, and methods discussed in reference 14, that monolayer coverage is achieved at $w/w_0 = 0.0002$. This is two orders of magnitude below the asymptotic weight gain, c .

In reference 11 an asymptotic, experimental decay expression is used to describe the oxidation of porous materials at temperatures too low for solid state diffusion to be important. According to that model the reaction ceases as products clog the pores of the material. In reference 7 the authors conclude that the rate of sulfation in the smaller pores of porous CaO is high but that they quickly become clogged. Thus, perhaps filling of the fine pores and cracks of this plasma sprayed material controls the initial sulfation kinetics. Asymptotic behavior could also be encountered if there were fine isolated islands of calcium silicate that could readily become saturated with reaction products. Other possible mechanisms for the early period could involve the initial formation of $\text{Ca}_3\text{Si}_2\text{O}_7$ ($n = 1/2$), or even CaSO_3 . Clearly, additional experiments, designed specifically to better characterize the early period, are required to fully understand the detailed mechanisms of the processes occurring at that time.

The fact that calcium silicate coatings are comparatively tolerant towards the effects of molten salts could be related to the sulfation process. That is, the reaction products could partially seal the surface of the coating thereby providing greater resistance to salt penetration. The presence of calcium sulfate could be detrimental to coating life if this substance hydrates or if it is soft. However, as discussed earlier, anhydrous calcium sulfate does not readily hydrate. In reference 4 the sulfation products were said to be soft. In the present study the sulfated specimens were not noticeably soft. However, in metallographically prepared specimens such as the one shown in Fig. 5, considerable pull-out is observed in the sulfated areas. Thus, if these areas are softer, then sulfated specimens may be more susceptible to erosion damage at high gas velocities.

CONCLUSIONS

Plasma sprayed calcium silicate reacts with the sulfur dioxide component of SO_2 /air mixtures to produce calcium sulfate plus less-calcium-rich calcium silicates. The reaction products form on the internal and external surfaces of the porous and microcracked coating material. The products affect the porosity of the material thereby influencing the reaction kinetics. At 900 and 1000°C and at high SO_2 levels the reaction rate is initially high, but decays exponentially with time. The rate in the subsequent period is low and decays exponentially with increasing weight gain. At lower SO_2 levels there is an initial period in which the reaction rate is governed by the rate of arrival of gaseous reactants to the surfaces of the calcium silicate. At 1100°C and at low SO_2 levels there is no reaction because under those conditions calcium silicate is more stable than the sulfation products. At 900 or 1000°C and at lower SO_2 levels and shorter times, the sulfation products are CaSO_4 plus $\text{Ca}_3\text{Si}_2\text{O}_7$. At higher SO_2 levels and longer times the products are CaSO_4 plus CaSiO_3 . These products can be rationalized by thermodynamic calculations for which the mole ratio of SO_2 to Ca_2SiO_4 reactants is treated as variable. The calculations also predict that CaSO_4 plus SiO_2 should form eventually. The sulfation products do not readily hydrate, but they may be somewhat softer than the original calcium silicate material.

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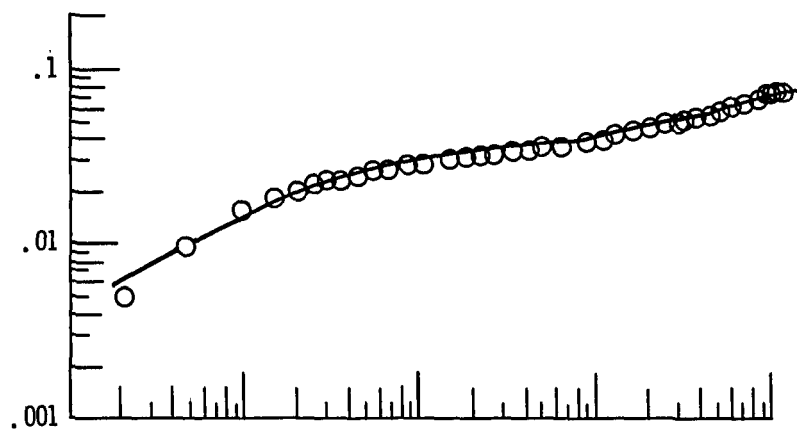
TABLE I. EXPERIMENTAL CONDITIONS AND DERIVED PARAMETERS FOR TEN SULFATION EXPERIMENTS.

Experiment Number	Temperature (°C)	%SO ₂	Time (hours)	w ₀ (mg)	Crucible Material	Air Flow Rate (cc/min NTP)
1	900	10.0	110	264	Pt	95
2	1000	10.0	112	289	Pt	95
3	900	0.53	102	1216	Pt	95
4	900	0.53	98	900	SiO ₂	95
5	1000	0.53	98	519	Pt	95
6	1000	0.53	507	1153	Pt	95
7	1000	0.53	25	392	Pt	95
8	900	0.036	393	364	Pt	100
9	1000	0.044	508	370	Pt	100
10	1100	0.036	2	352	Pt	100

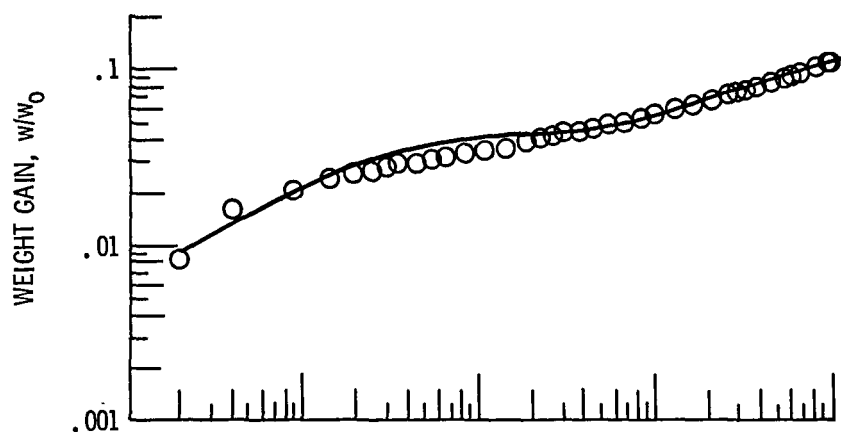
TABLE I. CONTINUED

Experiment Number	r ₀ (mg/hr)	r _s (mg/hr)	b	a (hr ⁻¹)	c	d (hr ⁻¹)
1	64*	651	0.0263	0.0357	0.0334	1.34
2	126*	651	0.0370	0.0624	0.0376	2.25
3	30	35	0.0155	0.104	0.0248	0.46
4	15	24	0.0102	0.170	0.0241	0.38
5	28	35	0.0114	0.104	0.0320	0.55
6	30	35	0.0213	0.0806	0.0324	0.33
7	28	35	--	--	--	--
8	2.2	2.9	0.0279	0.0484	0.0246	0.041
9	2.4	2.7	0.0209	0.0300	0.0368	0.073
10	0.0	2.9	0.0	0.0	0.0	0.0

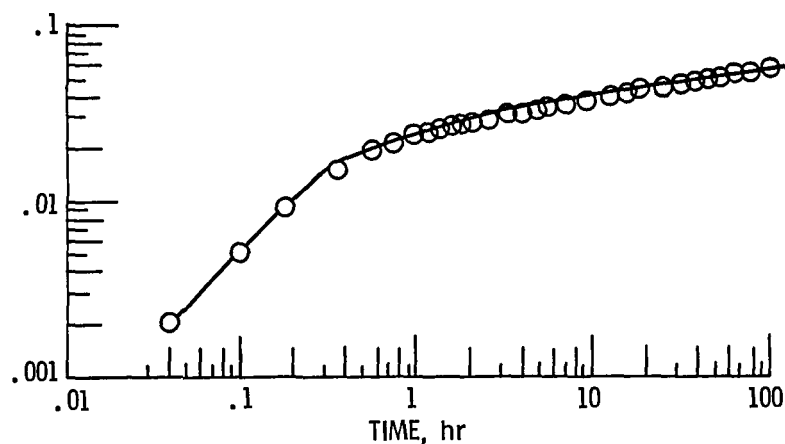
*Calculated from the weight gain at t = 0.2 hours and linearly extrapolated to zero.



(a) EXPERIMENT 1, 900° C, 10 percent SO₂ IN AIR.



(b) EXPERIMENT 2, 1000° C, 10 percent SO₂ IN AIR.



(c) EXPERIMENT 5, 1000° C, 0.53 percent SO₂ IN AIR.

Figure 1. - Weight gains vs. time showing experimental points \circ and analytical curve —. Curves (a) and (b) display a shoulder at short times. Curve (c) is linear at short times.

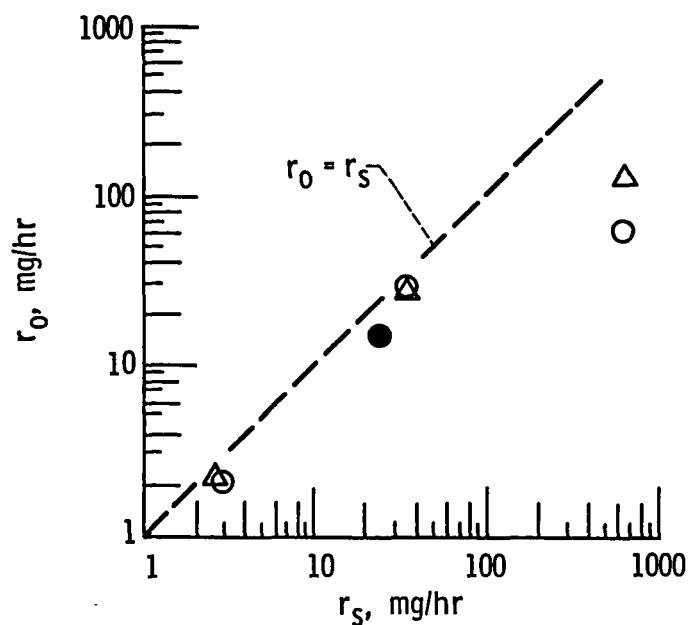


Figure 2. - Initial reaction rate, r_0 , vs. flow rate, r_s , of $\text{SO}_2 + 1/2 \text{O}_2$ at 900°C \circ and 1000°C \triangle using a platinum crucible, and at 900°C \bullet using a quartz crucible. (Data taken from table I.) For flow rates corresponding to < 0.53 percent SO_2 in air $r_0 \approx r_s$. Platinum catalysis of SO_2 to SO_3 does not significantly affect r_0 .

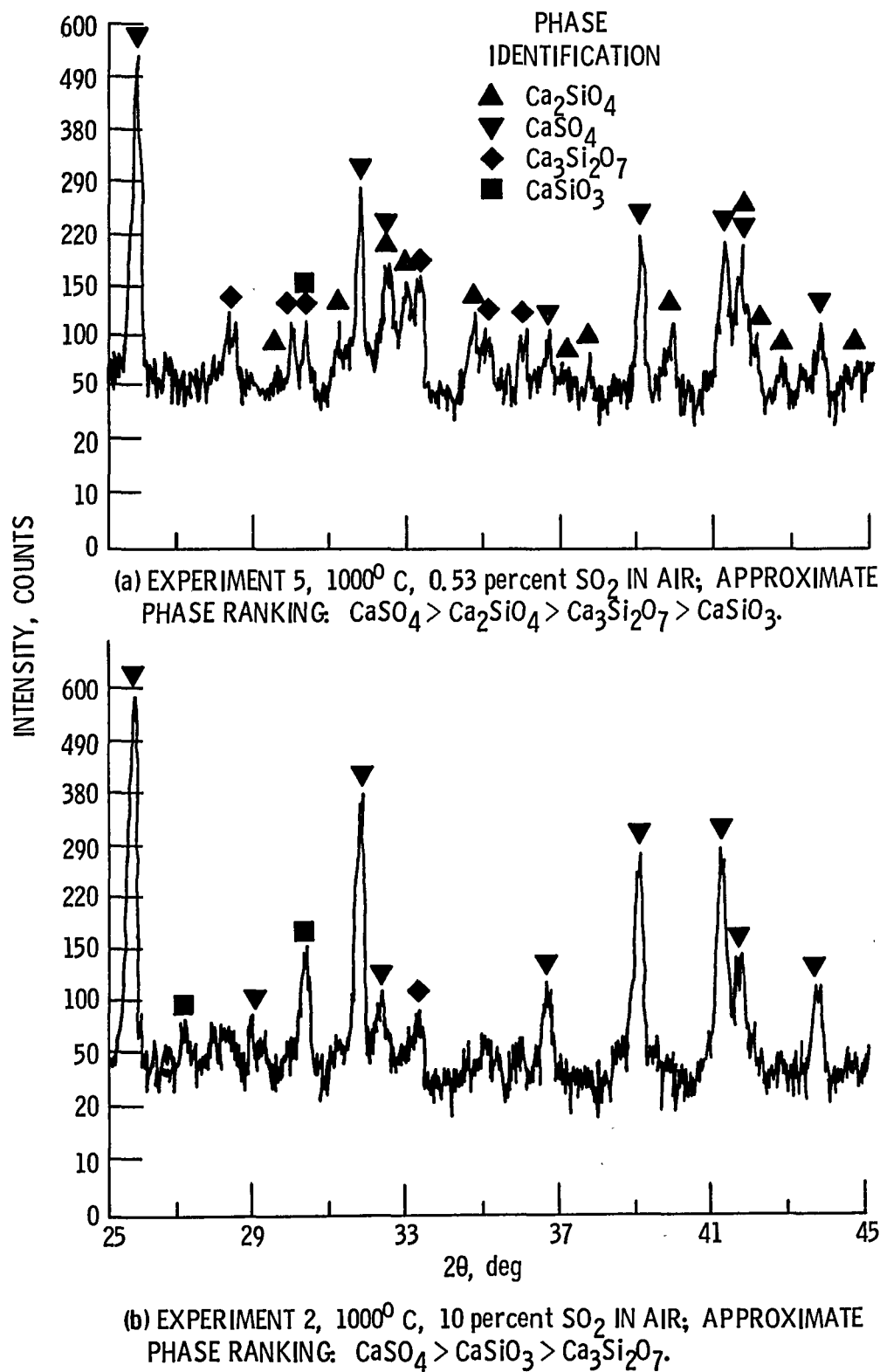
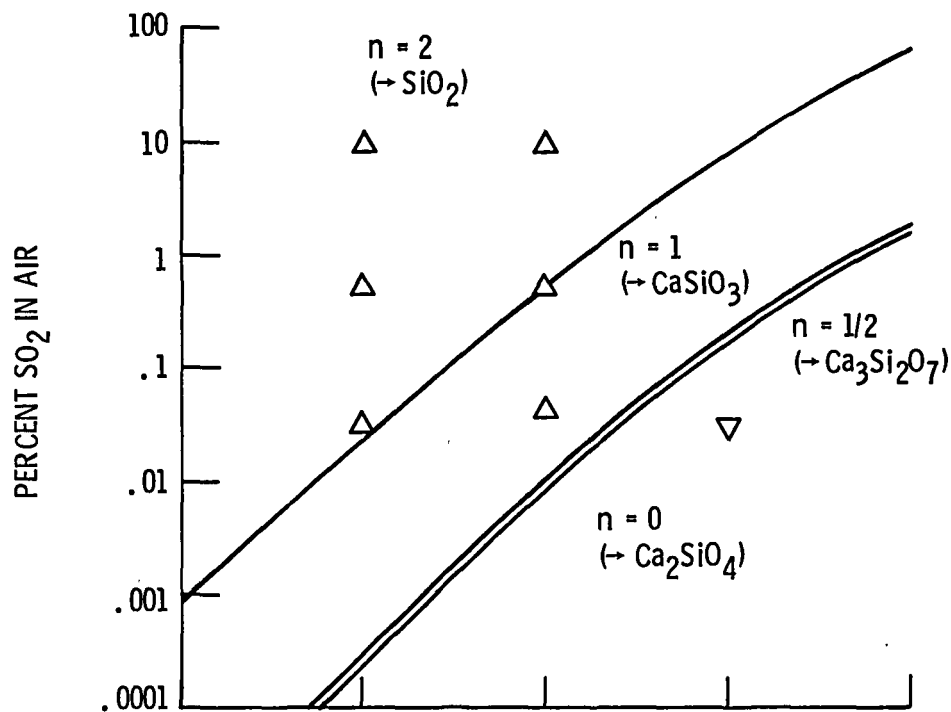
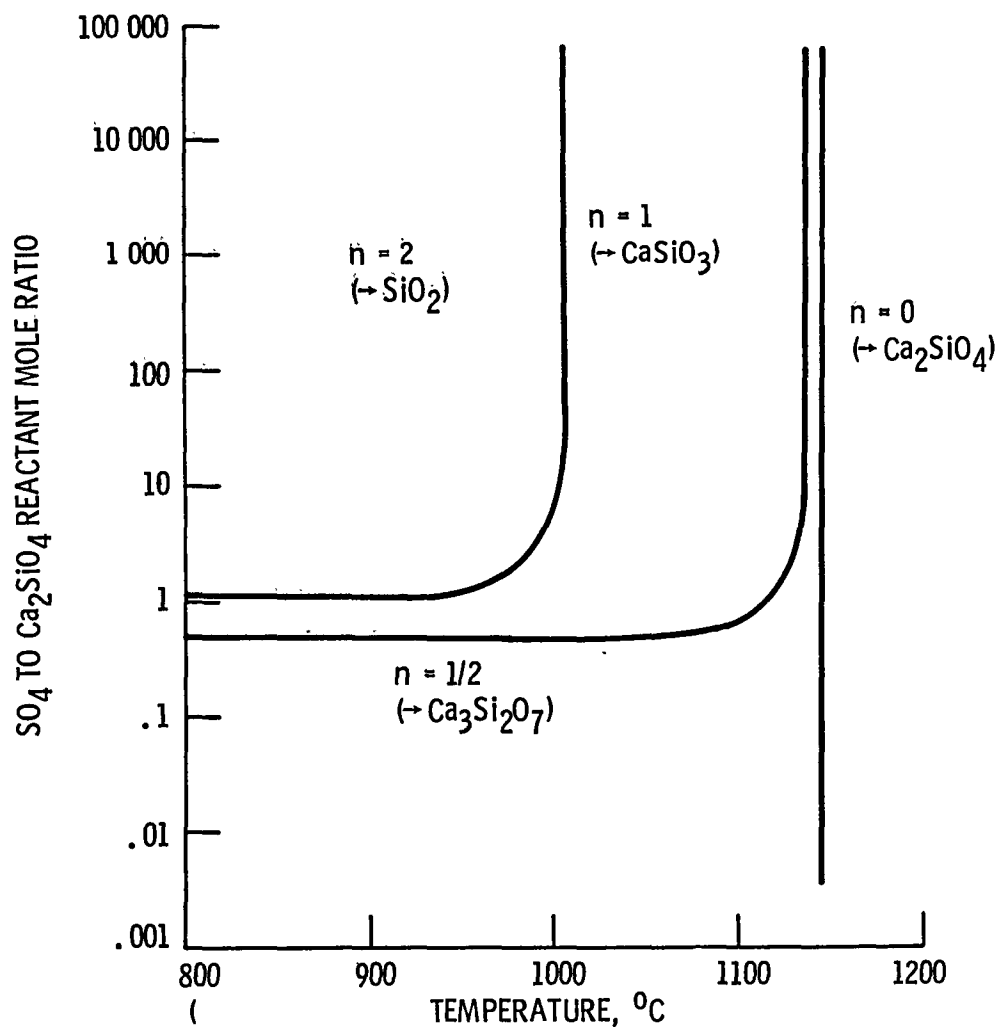


Figure 3. - Portion of X-ray diffraction pattern for sulfated calcium silicate.



(a) CALCULATED VALUES OF n AS A FUNCTION OF SO_2 LEVEL AND TEMPERATURE FOR A Ca_2SiO_4 LIMITED REACTION. (Δ) EXPERIMENTAL n APPROACHES $1/2$ AT LOWER SO_2 LEVELS AND SHORTER TIMES AND 1 AT HIGHER SO_2 , LONGER TIMES. (∇) AT HIGH TEMPERATURE, LOW SO_2 $n = 0$.

Figure 4. - Phase stability diagrams based on thermodynamic calculations showing moles SO_2 consumed (n) per mole of Ca_2SiO_4 . The predicted $(\text{CaO})_{2-n}\text{SiO}_4$ product is given in parentheses.



(b) CALCULATED VALUES OF n AS A FUNCTION OF SO₂ TO Ca₂SiO₄ REACTANT RATIO AND TEMPERATURE FOR 0.54 percent SO₂ IN AIR. EXPERIMENTAL REACTANT RATIOS INCREASE WITH INCREASING TIME.

Figure 4. - Concluded.

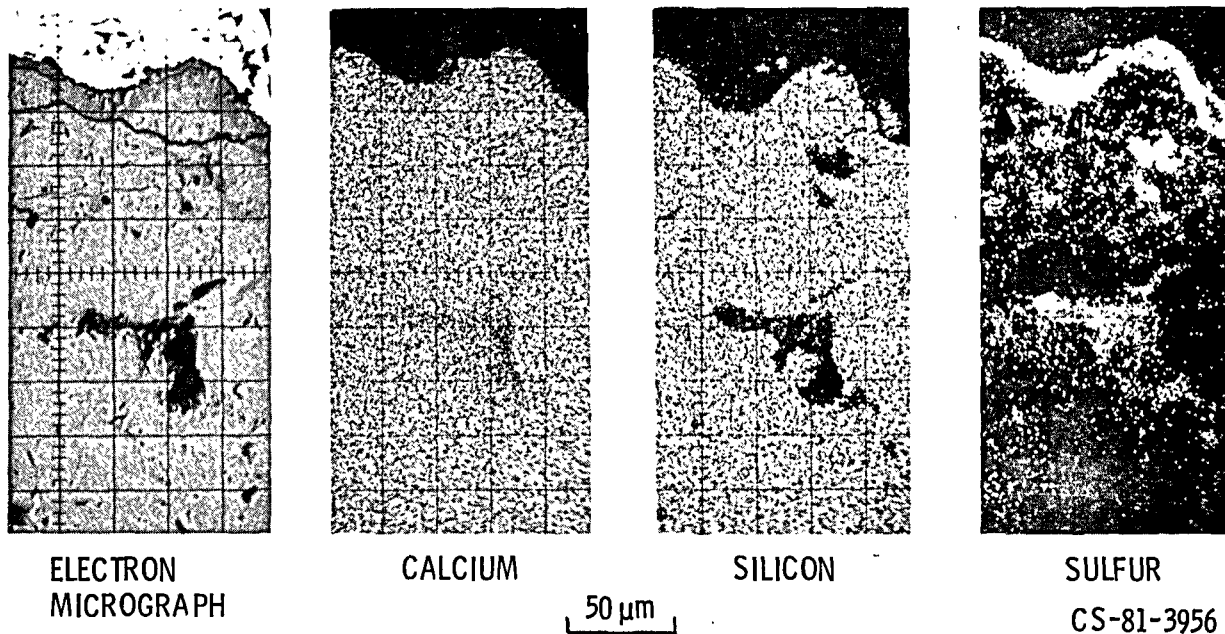


Figure 5. - Backscattered electron micrograph and X-ray maps of specimen cross sections from experiment 2, 1000⁰ C, 10% SO₂ in air. Sulfur is found on the external and internal surfaces of the material.

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